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Titanium oxide nanoparticles as additives in engine oil

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Abstract This research study investigates the tribological behaviour of titanium oxide (TiO_2) nanoparticles as additives in mineral based multi-grade engine oil. All tests were performed under variable load and varying concentrations of nanoparticles in lubricating oil. The friction and wear experiments were performed using pin-on-disc tribotester. This study shows that mixing of TiO_2 nanoparticles in engine oil significantly reduces the friction and wear rate and hence improves the lubricating properties of engine oil. The dispersion analysis of TiO_2 nanoparticles in lubricating oil using UV spectrometer confirms that TiO_2 nanoparticles possess good stability and solubility in the lubricant and improve the lubricating properties of the engine oil.

1. Introduction

One of the major losses occurring in the engine of an automobile is due to friction between its moving parts. This loss is significant and approximately 15% of the total loss of energy and has a direct impact on the efficiency and durability of the engine (Vadiraj et al., 2012). Different mechanical systems require a variety of functional lubricants to reduce the friction and wear of contacting surfaces as well as a significant reduction in the total energy consumed by mechanical systems. Lubricants play a major role in reducing the wear and friction between the two surfaces in contact with each other. Due to relative movement between the machine components, a resistive force called friction is developed which causes wear and tear of machine parts. Friction can be minimised by interposing a substance of low shear strength between the two moving surfaces. This phenomenon is known as lubrication and the interposed substance is called a lubricant. Hence, lubrication is fundamental to the operation of all engineering machines. Many studies have focused on improving the lubrication performance of general lubricants. One approach is to incorporate nanoparticle additives into regular lubricants so that it can reduce the friction and wear of frictional surfaces. The main function of a lubricant is to keep two metal surfaces wet thus minimising friction and avoiding wear (Calhoun, 1960). Research studies have reported that the nanoparticle dispersed lubricants are found to have a significant effect on reducing the friction and wear rate. It is also observed that the friction and wear also depend on the shape, size and concentration of the nanoparticles added in the lubricating oil. Vadiraj et al.

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(2012) investigated the effect of nano boric acid and nano copper based engine and transmission oil additives in different volume ratios on friction and wear performance of cast iron and case carburised gear steel. Wu et al. (2007) investigated the effect of additives CuO, TiO_2, and Nano-Diamond nanoparticles on the tribological properties of two different lubricating oils and observed that with CuO additive, oils significantly exhibited good friction-reduction and anti-wear properties. Thottackkad et al. (2012) studied the effect of Copper oxide nanoparticles as additive in the lubricating oil. Hwang et al. (2011) investigated the effect of size and morphology of nanoparticles suspended in lubricating oils on the lubrication performance. Zhang et al. (2009) also concluded from their research study that copper nanoparticles used as an oil additive improved the anti-wear and friction-reduction performance of lubricating oil. Choi et al.(2011) observed that the mixed nanofluids containing graphite and silver nanoparticles enhanced load-carrying and anti-wear properties in the FZG gear rig test and also reduced the electric-power consumption by more than 3% compared to the base oil. Hsin et al. (2011) investigated the tribological properties of the two-phase lubrication oil and nanodiamond–polymer composite. Based on the experiments it was observed that nanodiamond–polymer composite possessed better antiwear, friction-reduction and load-carrying capacity than the nanodiamond additive. Chu et al. (2010) experimentally investigated the anti-scuffing performance of nano-diamond-dispersed oil with various concentrations of diamond particles. A study conducted by Zin et al. (2013) with Cu nanoparticles as additive in lubrication oil reported that tribological properties of the oil were enhanced and coefficient of friction was found to be dependent on the size of Cu nanoparticles. It has been reported that the main mechanism of the friction reduction when nanoparticles were added can be attributed to rolling/sliding effect (Chin-as-Castillo and Spikes, 2003). Binu et al. (2014) studied the Influence of TiO_2 nanoparticle lubricant additive on the load carrying capacity of a journal bearing. The results showed an increase in the load carrying capacity of journal bearing using TiO_2 nanoparticle lubricant additive as compared to the oils without nanoparticle additive. Wan et al. (2015) conducted a study to understand the tribological properties of lubricant oil containing boron nitride nanoparticles. Through atomic force microscopic, scanning electron microscopy and X-ray energy dispersive spectroscopic analyses of element distributions on the worn surface they reported that the lubricant oil with a small amount of boron nitride nanoparticles exhibited excellent tribological performance behaviour. In this research study tribological properties of the lubricating oil were evaluated with the addition of TiO_2 nanoparticles using pin-on-disc tribometer under controlled conditions as per the ASTM standard G99 and the oil samples with dispersed TiO_2 nanoparticles were studied spectroscopically with the help of a UV spectrometer.

2. Experimental

In this study TiO_2 nanoparticles of grain size 10–25 nm were used as additive in mineral based multi-grade engine oil Servo 4T Synth 10W-30. The apparent density and the bulk density of TiO_2 nanoparticles were 0.3 g/cm^3 and 0.20 g/cm^3 respectively. The TiO_2 nanoparticles were purchased from Supplier Nanoshel LLC, USA. Aluminium alloy (LM 25) was used (Al-Si7Mg) as material for the pins to be used on pin-on-disc tribometer (see Table 1).

Table 1 Specifications of lubricating oil Servo 4T Synth 10W-30.

Density in kg m^{-3}	885
Viscosity at 100 °C in cSt	10–12
Viscosity at 40 °C in cSt	125.4
Viscosity index	150

A pin-on-disc type tribometer (DUCOM TR-20) was used to study the tribological properties of the lubricant. The tribometer consisted of a driven spindle and chuck for holding the revolving disc, a lever-arm device to hold the pin, and attachments to allow the pin specimen to be forced against the revolving disc specimen with a controlled load. The wear track on the disc was a circle, involving multiple wear passes on the same track. The tribometer also had a friction force measuring system (a load cell) to determine the coefficient of friction.

2.1. Fabrication of pin

The pins were fabricated from the aluminium alloy (LM 25) using manual labour techniques. The fabrication was done with the help of a cutting saw. The metal pieces were cut in triangular shapes and then cut metal piece were given a rough circular shape with the help of a hand grinder. The roughly circular aluminium pieces were then machined as per ASTM G99 size (10 mm diameter and 25 mm length) using lathe machine.

2.2. Preparation of nanolubricant

The TiO_2 nanoparticles were added to the lubricating oil at 0.3% wt, 0.4% wt and 0.5% wt. The required quantity of nanoparticles was accurately weighed using a precision electronic balance and mixed with the lubricating oil. A chemical shaker was used for mixing the nanoparticles uniformly in the lubricating oil. The time of agitation was kept as 30 min in order to prepare a stable suspension for sedimentation to begin.

2.3. Pin-on-disc tests

Tribological behaviour of the lubricating oil with and without the TiO_2 nanoparticles addition was evaluated using a pin-on-disc tribometer. Load, sliding speed and concentration of nanoparticles were considered as varying parameters for pin-on-disc tests. To determine the optimum concentration of nanoparticles, experiments were performed at different concentrations of TiO_2 nanoparticles in the oil.

The test parameters for pin-on-disc were considered in the following range:

- Load: 39.226 N, 49.033 N, 58.839 N.
- Sliding speed: 1.0 m/s.
- TiO_2 nanoparticles concentration (% weight): 0.3%, 0.4%, 0.5%.
- Sliding distance: 200 m.
- All the tests were carried out for a duration of 5 min.

Pins and disc were polished up to 600 grit size to make the surface flat and cleaned with acetone. Load was applied on pin by dead weight through pulley-string arrangement. Lubricant was applied between the pin and disc to satisfy boundary lubrication conditions. Frictional force was measured from the controller and weight loss of the pin was measured using electronic weighing balance (accuracy of 0.1 mg). The above procedure was repeated for all the tests. The specimens were cleaned and dried. All dirt and foreign matters were removed from all the specimens before starting the experiment. Non chlorinated, non-film-forming cleaning agents and solvents were used. The disc was inserted carefully in the holding device so that it remained perpendicular to the axis of the resolution. The pin specimen was inserted in the holder and adjusted to make it perpendicular to the disc surface when in contact to maintain the necessary contact conditions. Proper mass was added to the system lever to the selected force pressing the pin against the disc. The electric motor was started and the speed of the disc was adjusted to the desired value. The revolution counter was set to the desired number of revolutions. The experiment started with the specimens in contact under load. The test was stopped when the desired numbers of revolutions were achieved. The specimen was removed and cleaned. The existence of features on or near the wear scar such as: protrusions, displaced metal, discoloration, micro cracking, or spotting were noted. The tests were repeated with additional specimens to obtain sufficient data for statistically significant results. The WinDucom software was used for data acquisition and display of results.

The WinDucom instrumentation and data acquisition were used to measure RPM, wear, and frictional force.

2.4. Dispersion analysis using UV spectrometer

The oil samples with TiO_2 nanoparticles were spectroscopically studied for the dispersion and stability of nanoparticles in the lubricating oil. UV Spectrometer was employed for dispersion analysis of the TiO_2 nanoparticles in the lubricating oil. Base oil (lubricating oil without TiO_2 nanoparticles) was filled in two cuvettes and baseline correction was done. In one cuvette the lubricant with 0.3% wt TiO_2 nanoparticles additive was filled while other cuvette was filled with base oil without any additive. The absorption of light through the lubricating oil with TiO_2 nanoparticles 0.3% wt was measured over a range of wavelengths. The absorption of light was found to be proportional to the dispersion of TiO_2 nanoparticles in the oil. The procedure was repeated by taking lubricating oil with 0.5% wt dispersed TiO_2 nanoparticles.

3. Results and discussion

3.1. Dispersion analysis using UV spectrometer

In the present work, UV spectroscopy was carried out using 3 samples of lubricating oil with dispersed TiO_2 nanoparticles at concentrations of 0.3%, 0.4% and 0.5% wt. The UV spectroscopy measurements were done by directly taking the samples in a short path-length measurement cell. The UV spectrometry studies of the samples showed a steady absorbance increase with an increase in ageing time; and a spectral shift from short to longer wavelength in the course of oil ageing was noticed. Optical maximum-absorbance (absorbance maxima) of the samples and its wavelength of occurrence also increased with ageing time. Hence, it can be concluded that the shift in the absorbance spectra was associated with a shift in maximum-absorbance wavelength from short to longer wavelength. The TiO_2 nanoparticles used as additives in lubricating oil showed good stability and solubility in the lubricant. They were observed to be readily dispersed in lubricating oil to give a transparent solution, and the solution remained unchanged for several days at room temperature.

3.2. Tribological tests results on pin-on-disc tester

A series of experiments were conducted to evaluate the friction and wear characteristics of the sliding elements using pin-on-disc tribometer applying the lubricant at the interface (for a sliding distance of 600 m) with and without the TiO_2 nanoparticles in the lubricating oil. It was observed that coefficient of friction varied with the increase in load for lubricating oil without TiO_2 nanoparticles (Fig. 1). The variation in coefficient of friction for a given time duration of 0–300 s was observed to be more for the load of 4 kg in comparison with 5 kg or 6 kg loads.

Table 2 shows that the coefficient of friction was significantly reduced when 0.3% wt TiO_2 nanoparticles were added in the lubricating oil for the given load. A decrease in COF was observed to be 86.48%, 78.04% and 34.50% for the loads 4 kg, 5 kg and 6 kg respectively. The reduction in COF was the maximum for the smallest load 4 kg and minimum for the largest load 6 kg.

Fig. 2 shows the variation in COF with time for the lubricating oil with 0.3% wt TiO_2 nanoparticles and also compares with oil without TiO_2 nanoparticles at load values 4, 5 and 6 kg respectively. It indicates that there is a significant reduction in COF for lubricating oil with 0.3% wt TiO_2 nanoparticles at 4 kg load.

Fig. 3 shows the variation in COF with time for the lubricating oil with 0.4% wt TiO_2 nanoparticles and also compares the COF of oil without TiO_2 nanoparticles at load values 4 and

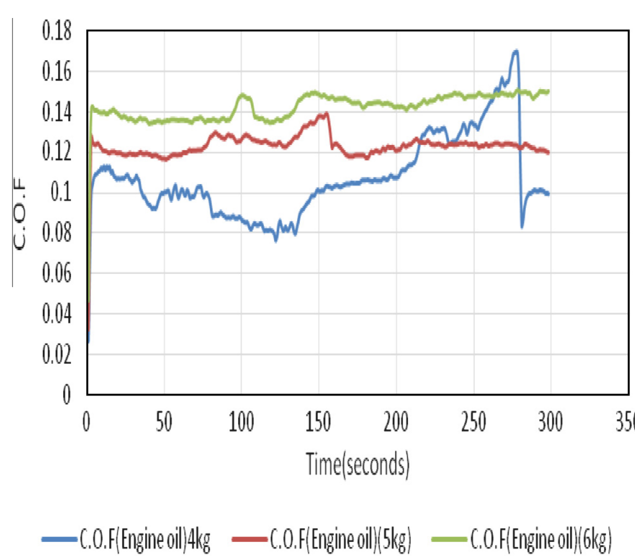

Figure 1 Showing variation of COF with time for lubricating oil without TiO_2 nanoparticles.

Table 2 Comparison of coefficient of friction between lubricating oil without and with 0.3% wt TiO_2 nanoparticles for loads 4 kg, 5 kg & 6 kg loads.

Load (kg)/force (N)	Coefficient of friction (engine oil)	Co efficient of friction (engine oil + 0.3% wt TiO_2 nanoparticles)	Percentage decrease (%)
4/39.226 N	0.111	0.015	86.48
5/49.033 N	0.123	0.027	78.04
6/58.839 N	0.142	0.093	34.50

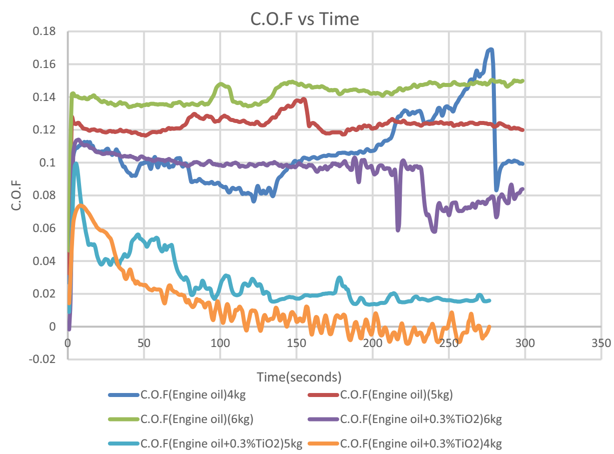

Figure 2 Variation in co-efficient of friction of lubricating oil with 0.3% wt TiO_2 nanoparticles.

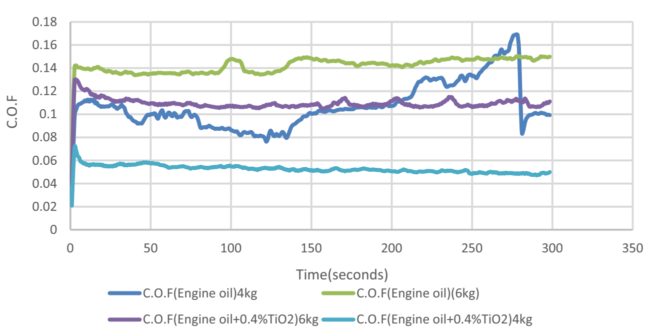

Figure 3 Variation in co-efficient of friction of lubricating oil with 0.4% wt TiO_2 nanoparticles.

6 kg respectively. The reduction in COF was observed to be maximum for lubricating oil with 0.4% wt TiO_2 nanoparticles at load 4 kg.

Fig. 4 shows the decrease in COF of lubrication oil when 0.5% wt TiO_2 nanoparticles were dispersed in it for loads 4 kg, 5 kg and 6 kg. Table 4 indicates that there is considerable decrease in CFO with 0.5% additive. This study shows that mixing of TiO_2 nanoparticles in lubricating oil significantly reduces the friction and wear rate and hence improves the lubricating properties; TiO_2 nanoparticles were dispersed in lubricating oil as additives. It was demonstrated that the nanoparticles as additives in lubrication can effectively improve the lubricating properties.

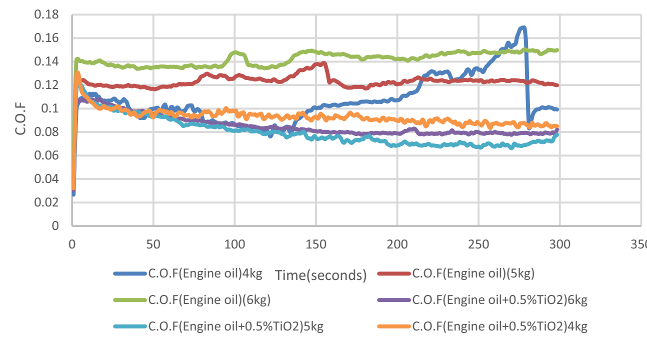

Figure 4 Variation in co-efficient of friction of lubricating oil with 0.5% wt TiO_2 nanoparticles.

Table 3 shows the comparison between the COF for lubricating oil with 0.4% wt TiO_2 nanoparticles as additives and without an additive. It was observed that there was a decrease in COF with 0.4% wt TiO_2 nanoparticles as additives in lubricating oil. 52% and 23% reduction in COF was observed for loads 4 kg and 6 kg respectively when 0.4% wt TiO_2 nanoparticles were dispersed in the lubricating oil.

Fig. 5 shows the variation in wear with the applied load of the sample pins which were fabricated from the aluminium alloy (LM 25). It was observed that the wear of the pin increased with time. The wear rate was observed to be increasing with the load for lubricating oil without TiO_2 nanoparticles as well as with TiO_2 nanoparticles as additive. However the increase in wear with time was observed to be more in case of lubricating oil without TiO_2 nanoparticles. With the addition of 0.3% TiO_2 nanoparticles, there was a decrease in the wear of the pin and the reduction was observed maximum when the load of 5 kg was applied.

Fig. 6 shows the variation in wear with the applied load of the sample pins which were fabricated from the aluminium alloy (LM 25). It was observed that the wear of the pin increased with time. The wear rate was observed to be increasing with the load for lubricating oil without TiO_2 nanoparticles as well as with TiO_2 nanoparticles as additives. However the increase in wear with time was observed to be more in case of lubricating oil without TiO_2 nanoparticles. With the addition of 0.4% wt TiO_2 nanoparticles, there was a decrease in the wear and the maximum reduction in the wear was observed at load 4 kg in the oil with 0.4% wt TiO_2 nanoparticles as additive.

Fig. 7 shows the variation in wear with the applied load of the sample pins which were fabricated from the aluminium alloy (LM 25). It was observed that the wear of the pin increased with time. The wear rate was observed to be increasing with the load for lubricating oil without TiO_2 nanoparticles as well as with

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Table 3 Comparison of coefficient of friction between lubricating oil without additive and with 0.4% wt TiO_2 nanoparticles for loads 4 kg & 6 kg.

Load (kg)/force (N)	Co efficient of friction (engine oil)	Co efficient of friction (engine oil + 0.4% TiO_2)	Percentage decrease (%)
4/39.226 N	0.111	0.053	52
6/58.839 N	0.142	0.109	23

Table 4 Comparison of coefficient of friction between lubricating oil without TiO_2 nanoparticles as additive and with 0.5% wt TiO_2 nanoparticles as additive for loads 4 kg, 5 kg & 6 kg.

Load (kg)/force (N)	Co efficient of friction (engine oil)	Co efficient of friction (engine oil + 0.5% TiO_2)	Percentage decrease (%)
4/39.226 N	0.111	0.093	16.2
5/49.033 N	0.123	0.080	34.2
6/58.839 N	0.142	0.085	40.1

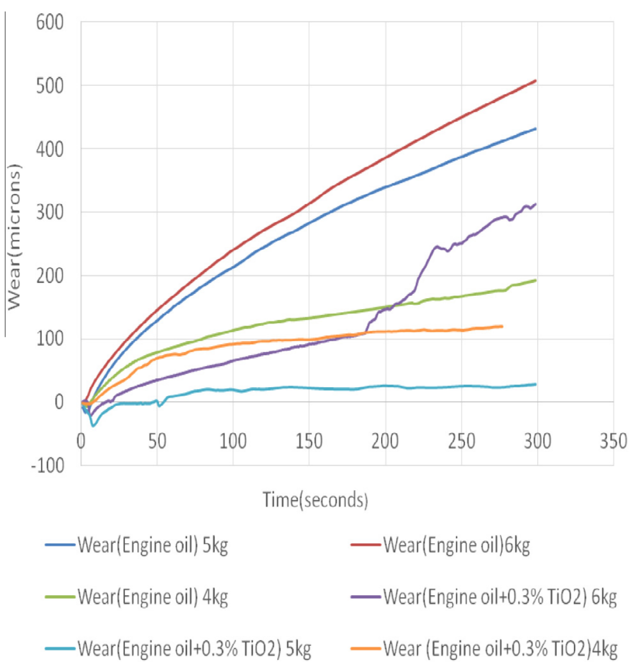

Figure 5 Wear of (LM 25) alloy with lubricating oil and with 0.3% wt TiO_2 nanoparticles as additives at varying loads.

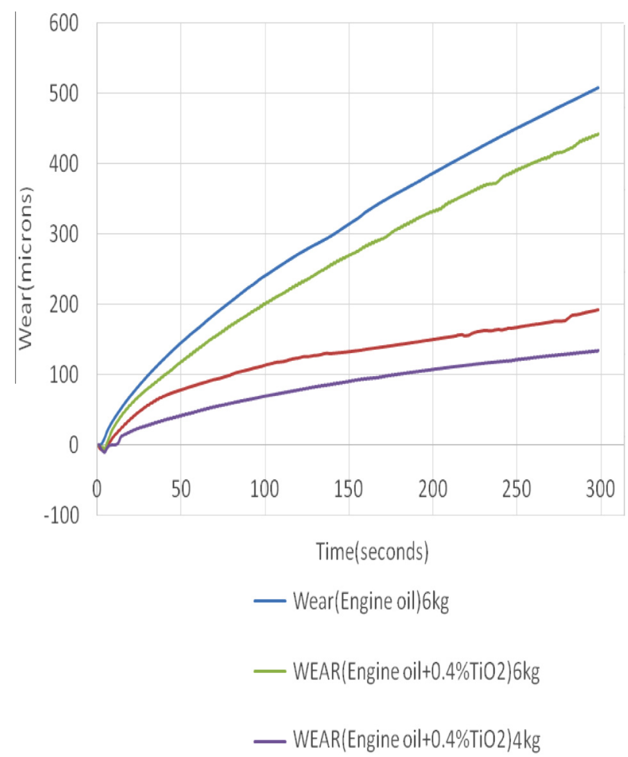

Figure 6 Wear of (LM 25) alloy with lubricating oil and with 0.4% wt TiO_2 nanoparticles as additives at varying loads.

TiO_2 nanoparticles as additive. However the increase in wear with time was observed to be more in case of lubricating oil without TiO_2 nanoparticles. With the addition of 0.5% wt TiO_2 nanoparticles, there was a decrease in the wear of the pin and the reduction was observed maximum when the load of 4 kg was applied.

The experimental results obtained from pin-on disc tribometer tests indicate the enhanced anti friction and anti-wear properties of TiO_2 nanoparticles as additives in the lubricating oil. UV spectroscopy results show that the addition of TiO_2 nanoparticles into the lubricating oil forms a stable and homogeneous solution. The role of TiO_2 nanoparticles in enhancing the anti friction and anti wear properties of the lubricating oil can be understood by knowing that when the lubricating film between the mating pairs becomes thinner, the TiO_2 nanoparticles carry a proportion of load and prevent the two surfaces from rubbing between the mating pair thereby showing the anti-friction and anti-wear properties. According to the theory of tribology, during mixed or boundary layer lubrication conditions, nanoparticles as additives may generate a tribo-film through deposition mechanism. Since nanoparticles are smaller or similar in size compared to the film thickness, they penetrate and deposit on the mating surface. This reduces the material consumption from the mating surfaces. Continuous formation and wear off of the tribo-films occurs

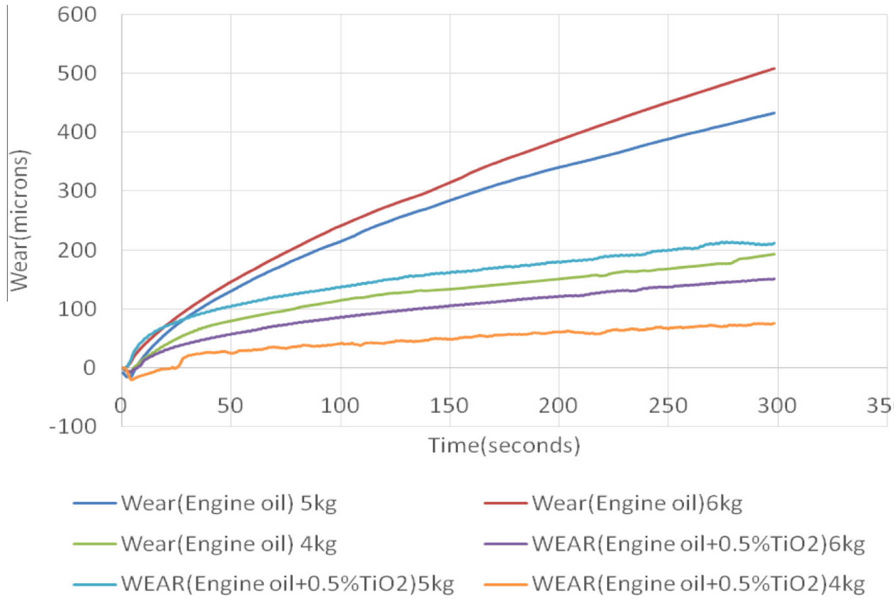

Figure 7 Wear of (LM 25) alloy with lubricating oil and with 0.5% wt TiO_2 nanoparticles and without TiO_2 nanoparticles at varying loads.

at the interface of mating surfaces. It can be inferred that the nanoparticles as additives in lubrication can effectively improve the lubricating properties. Another phenomenon which supports the above statement is that the nanoparticles present in between the mating surfaces help to convert the sliding friction into rolling friction which results in the reduction of the friction coefficient.

4. Conclusion

Tribological properties of lubricating oil were enhanced due to the addition of TiO_2 nanoparticles. TiO_2 nanoparticles used as additives in the lubricating oil exhibited good friction reduction and anti-wear behaviour. When TiO_2 nanoparticles were added to the engine oil, the co efficient of friction was reduced by 86% with 0.3% concentration by weight of the oil as compared to the oil without TiO_2 nanoparticles for load 4 kg. This effect could be due to the rolling of the sphere like nanoparticles between the rubbing surfaces, thus reducing friction. With an increasing concentration of nanoparticles the co-efficient of friction increased but not more than the coefficient of friction of oil without TiO_2 nanoparticles, this effect can be observed due to the agglomeration of TiO_2 nanoparticles. The anti-wear mechanism can be attributed to the deposition of TiO_2 nanoparticles on the worn surface, which in turn decreased the shearing resistance, thus improving the tribological properties. Nanoparticles can be considered as nano-bearings on the rubbing surfaces. The TiO_2 nanoparticles are deposited only under mixed and boundary lubrication. Experimental studies report that the deposition of TiO_2 nanoparticles on the rubbing surfaces improves the tribological properties of the base lubrication oil exhibiting reduction in friction and wear.

The wear of Aluminium alloy (Al 25) with time was observed to be increasing with an increased value of the load. However the wear was significantly reduced with TiO_2 nanoparticles as additives for the same load value. Thus, TiO_2 nanoparticles can be used as a multifunctional additive. The UV spectroscopic study indicates that TiO_2 nanoparticles possess good stability and solubility in the lubricant.

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